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Adducts of Bis(salicylaldehydato) Ni(II) with Some Organic Bases & Ni(II) Complexes of Schiff Bases Derived from Salicylaldehyde & 2- & 3-Aminopyridines

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Diaquobis(salicylaldehydato) Ni(II) reacts with organic bases like pyridine, β-picoline, 2-, 3- and 4-aminopyridines and quinoline to form diaminobis(salicylaldehydato) Ni(II). The adducts are non-electrolytic and have been assigned distorted octahedral geometry on the basis of electronic and magnetic moment data. Ni(II) forms complexes with Schiff bases derived from 2- and 3-aminopyridines and salicylaldehyde to give compounds of the types $Ni(Sal.L')_2H_2O$ (where Sal.L′ = Schiff base derived from salicylaldehyde and 2-aminopyridine) and $Ni(Sal.L'')_2$ (where Sal.L″ = Schiff base derived from salicylaldehyde and 3-aminopyridine). The compounds are suggested to be polymeric octahedral complexes involving ligand bridges.

MANY Ni(II) complexes of salicylaldehydes[1,2] and their Schiff bases with various amines[3] have been reported in literature. The *trans* octahedral adducts of bis(salicylaldehydato) Ni(II) with water and pyridine (in solid state) and with γ-picoline (in solution) have been studied. The *cis* octahedral geometry has been observed with *o*-phenanthroline adducts[1,2].

This paper describes the preparation, magnetic and spectral properties of pyridine (and its derivatives) and quinoline adducts of salicylaldehydato complex of Ni(II) and Ni(II) complexes of Schiff bases derived from salicylaldehyde and 2- and 3-aminopyridines. Literature survey shows that such complexes have not been studied in solid state excepting dipyridine bis(salicylaldehydato) Ni(II) (ref. 1).

Materials and Methods

All the chemicals were of CP grade and the solvents were purified before use.

Preparation of pyridine/quinoline adductso f bis-(salicylaldehydato)Ni(II)[$(Ni(Sal)_2L_2$]—$Ni(Sal)_2(H_2O)_2$ was suspended in ethanol, warmed, stoichiometric quantity of the required amine (dissolved in ethanol) added to it and the whole mixture refluxed for 30 min. Compounds containing pyridine, β-picoline and quinoline were obtained by slow evaporation of the solution *in vacuo*. 2-Aminopyridine adduct appeared rather quickly, whereas those of 3- and 4-aminopyridines were obtained on slow evaporation. The compounds were washed with a small quantity of benzene and dried *in vacuo*. α-Picoline and 2-methylquinoline adducts could not be isolated in pure state. 4-Aminopyridine adduct separated as emerald-green solid which changed after filtration to any ellowish green micro-crystalline compound. The unstable intermediate could not be identified but the end product has the composition of a diamine adduct.

Preparation of Ni(II) complexes of Schiff bases derived from salicylaldehyde and 2-aminopyridine (L′) and 3-aminopyridine (L″) [$Ni(Sal.L')_2H_2O$ *and* $Ni(Sal.L'')_2$] — Stoichiometric amounts of salicylaldehyde and the required aminopyridine were refluxed together for 1 hr. The resulting viscous liquid was added to ethanolic solution of anhydrous Ni(II) chloride and the mixture refluxed further for 1 hr. The solid obtained was filtered, washed with ethanol and ether and then dried *in vacuo*. In the case of 4-aminopyridine a mixture of red and yellowish green compounds of non-uniform composition was obtained.

Results and Discussion

The analytical data, melting points, molar conductances in acetone and magnetic susceptibility data (determined by Gouy method) are recorded in Table 1.

TABLE 1 — COLOUR, MELTING POINT, ANALYTICAL, CONDUCTANCE AND MAGNETIC DATA OF THE COMPLEXES

Compound	Colour	m.p. (°C)	Ni (%)†
$Ni(Sal)_2Py_2$	Yellowish green	125	12·1 (12·7)
$Ni(Sal)_2(\beta\text{-Pic})_2$	Light brown	177	12·0 (12·07)
$Ni(Sal)_2Q_2$	Yellowish green	200d	10·3 (10·5)
$Ni(Sal)_2(2\text{-AmPy})_2$	do	174	11·9 (12·02)
$Ni(Sal)_2(3\text{-AmPy})_2$	do	200d	12·0 (12·02)
$Ni(Sal)_2(4\text{-AmPy})_2$	do	220d	12·0 (12·02)
$Ni(Sal\text{-}2\text{-}AmPy)_2H_2O$*	Green	235d	12·3 (12·48)
$Ni(Sal\text{-}3\text{-}AmPy)_2$	Yellow	210d	12·7 (12·97)

*H_2O (Found 3·7; reqd 3·82%).
†Values in the parentheses indicate required values.

The adducts, $Ni(Sal)_2L_2$, are soluble in most of the organic solvents. Amongst the Schiff base complexes, $Ni(Sal.L')H_2O$ is only slightly soluble in acetone, methanol etc., whereas $Ni(Sal.L'')_2$ is insoluble in most of the organic solvents.

The TIP corrected magnetic moments of the compounds are found to be in the range 3·10-3·19 B.M. and the approximate g-values are calculated to be in the range 2·19-2·26. These values are consistent with a high spin octahedral configuration[4-6] for the Ni(II) ion. The spin-orbit coupling constant (λ) lies in the range 175-258 cm^{-1} for Ni(II) complex as against free-ion value (λ_0) of 324 cm^{-1}. Consequently the covalency parameter (γ) comes to be in the range 0·69-0·80 (ref. 5, 6).

The IR spectrum of the starting compound, $Ni(Sal)_2(H_2O)_2$, shows ν(O—H) at 3460 cm^{-1} which disappears in the spectra of its adducts indicating replacement of water molecules by amine molecules. ν(C=O) band appearing at 1540 cm^{-1} in the parent compound[7,8] shifts to ~1510 cm^{-1} in the adducts. ν(N—H) vibrations of the amine remain undisturbed at ~3300 cm^{-1} (ref. 7) in aminopyridine adducts indicating their non-involvement in bonding.

The pKa (LH^+) values of the hetero-ligands (L) are found to have more or less linear relationship with ν(C=O) of the adducts, suggesting correlation between the electron donor property of the hetero-ligand and the carbonyl bond order of salicylaldehyde moiety and hence the metal-carbonyl oxygen bond strength. This can be explained on the basis of electronic charge accumulation over the ligated metal ion. Similar correlation between pKa and ν(M—O) have been observed for some β-diketone complexes[9].

The absence of ν(N—H) vibrations[7] around 3300 cm^{-1}, the presence of ν(C=N)[7,10] around 1620 cm^{-1} [mixed with ν(C=C)] and the absence of ν(C=O) bands around 1520 cm^{-1} in the spectra of $Ni(Sal.L')H_2O$ and $Ni(Sal.L'')_2$ confirm Schiff base formation. The Schiff base complex derived from 2-aminopyridine shows a broad band at 3450 cm^{-1}, possibly due to coordinated water[7,8], whereas that derived from 3-aminopyridine has no such water band. It may be pointed out that the phenolic ν(C—O) in the adducts, $Ni(Sal)_2L_2$, and in the Schiff base complex derived from 2-aminopyridine occur more or less at the same position, whereas there is a decrease of ~62 cm^{-1} in the position of ν(C—O) in the Schiff base complex derived from 3-aminopyridine.

The general pattern of electronic absorption bands and the ν_2/ν_3 ratios (~1·60) are in agreement with an octahedral symmetry for the present complexes. Besides ν_1 (=10,000 cm^{-1}) and ν_2 (~16,000 cm^{-1}) bands, we get weak bands or shoulders around 13,000 cm^{-1}, possibly due to the spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ transition[11]. The values of ν_3 (~29,000 cm^{-1}), Racah (B, 956-990 cm^{-1}) and naphelauxetic (β_{35}, 0·89-0·91) parameters also indicate the presence of large covalency in the present molecules. The intense bands occurring in the range 22,830-25,000 cm^{-1} are perhaps charge-transfer bands, possibly enveloping ν_3 absorption band. Additional bands around 25,000 cm^{-1} in Schiff base complexes are perhaps due to charge-transfer involving the azomethine group.

On the basis of above analytical and spectral data, distorted octahedral structures are suggested for the present compounds. In the case of Schiff base complexes where metal: ligand ratio is 1:2, hexacoordination is achieved by coordination of the central metal ion with nitrogen atoms of the neighbouring molecules, forming an overall polymeric structure. In the case of $Ni(Sal\text{-}2\text{-}AmPy)_2H_2O$, one site of coordination is occupied by the water molecule in the polymeric structure.

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References

1. Graddon, D. P., *Coord. chem. Rev.*, **4** (1969), 1.
2. Graddon, D. P. & Mockler, G. M., *Aust. J. Chem.*, **20** (1967), 21.
3. Holm, R. H., Everett (Jr), G. W. & Chakravorty, A., *Progress in inorganic chemistry*, Vol. VII (Interscience, New York), 1966.
4. Cotton, F. A. & Wilkinson, G., *Advanced inorganic chemistry* (Interscience, New York), 1966.
5. Figgis, B. N., *Introduction to ligand fields* (Interscience, New York), 1966.
6. Lakshman, S. V. J. & Rao, J. L., *Indian J. pure appl. Phys.*, **9** (1971), 139.
7. Nakamoto, K., *Infrared spectra of inorganic and coordination compounds* (John Wiley, New York), 1963.
8. Dey, K. & Ray, K. C., *J. Indian chem. Soc.*, **50** (1973), 66.
9. Haigh, J. M., Slabbert, N. P. & Thronton, D. A., *J. inorg. nucl. Chem.*, **32** (1971), 3635; Weedenheft, C. J., *Inorg. nucl. chem. Lett.*, **7** (1971), 439.
10. Kovacic, J. E., *Spectrochim. Acta*, **23A** (1967), 183.
11. Misra, M. K. & Ramana Rao, D. V., *J. inorg. nucl. Chem.*, **34** (1972), 782.